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SUBJECT: Cathodes Developed by Robert Dopp

ABSTRACT: Over my 30+ years working in air cathode development, several generations of electrodes were developed[1]. All of them used a form of nickel as the structural current collector and various types of coal-based activated carbon as the reactive surface. Catalysts were always some form of MnO_x with varying methods of distribution and size. Machines were designed and built to control the compression of the components with precision. Five production cathode manufacturing machines were designed and built for four different entities.

Overview: The oxygen electrode consumes ambient oxygen in a gas diffusion electrode by the reaction of: $\frac{1}{2}O_2 + H_2O + 2e^- \rightarrow 2OH^-$ where the hydroxyl is typically used as the charge-carrier in a metal air battery such as zinc air or magnesium air chemistry where the hydroxyl oxidizes the metal, liberating a pair of electrons and a water molecule by: $Zn + 2OH^- \rightarrow ZnO + H_2O + 2e^-$. The water returns to the cathode to be oxidized once again. In some instances, the hydroxyl is used for other chemical reactions.

Construction: The air cathodes described here are all similar in general design. **Figure 1** shows this construction. The secondary sheet of Teflon film is only present in the cell, but not in half-cell testing. The separator is also not included in half-cell testing except when the characteristics of the separator and adhesive are being studied. The Current Collector is sometimes cross-bonded nickel screen and sometimes fine-gauge expanded nickel.

The "Active Layer" is a coal-based activated carbon, which has a very large internal void volume. Into this cavernous labyrinth, nano-sized particles of the catalyst are deposited. Some methods include using a soluble form of manganese, then reducing it to grow the manganese particles *in situ* where they spontaneously oxidize into a use-

Figure 1: General cathode construction

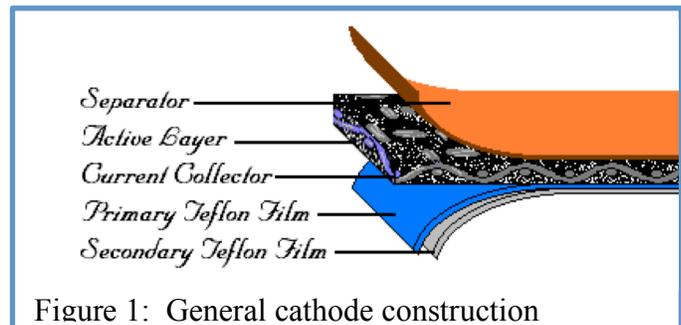ful form of MnO_x (predominantly β MnO_2). Another very effective method is to add nano-sized MnO_x to a very wet slurry of the carbon and mix in a laminar way. Then a Teflon emulsion is then used to render the active mix hydrophobic – but in a fibrillated mass rather than in a uniform coating. This allows for moisture to penetrate into the active mass, but with dry, oxygen conducting micro-tubes running throughout the mass. The carbon is conductive, so where the oxygen meets the water on a conductive surface (a "triple-phase interface") the oxygen reduction reaction can proceed.
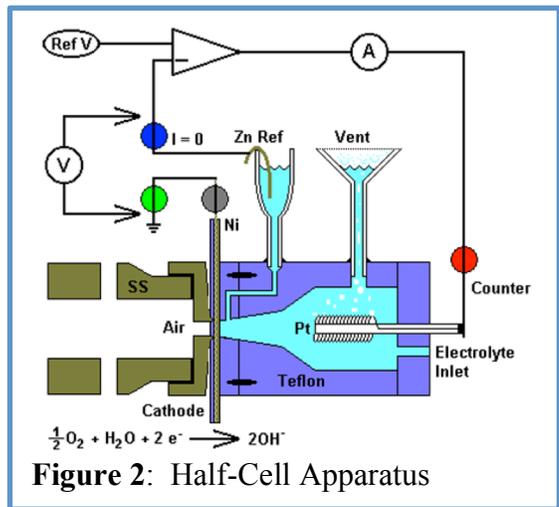
The **design criterions** that matter include:

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[1] My sincere thanks to the many talented co-workers and colleagues who have contributed to these efforts. No development occurs in a vacuum.

- The activated carbon source and method of activation
- Catalyst loading method
- Additives to improve electrical conductivity
- Teflon emulsion loading and method of application
- Pre-conditioning of the dried active mix
- Compression of the mix causing fibrillation
- Additives to increase ionic conductivity within the matrix
- Pre-treatment of the current collector
- The type of Teflon film used and
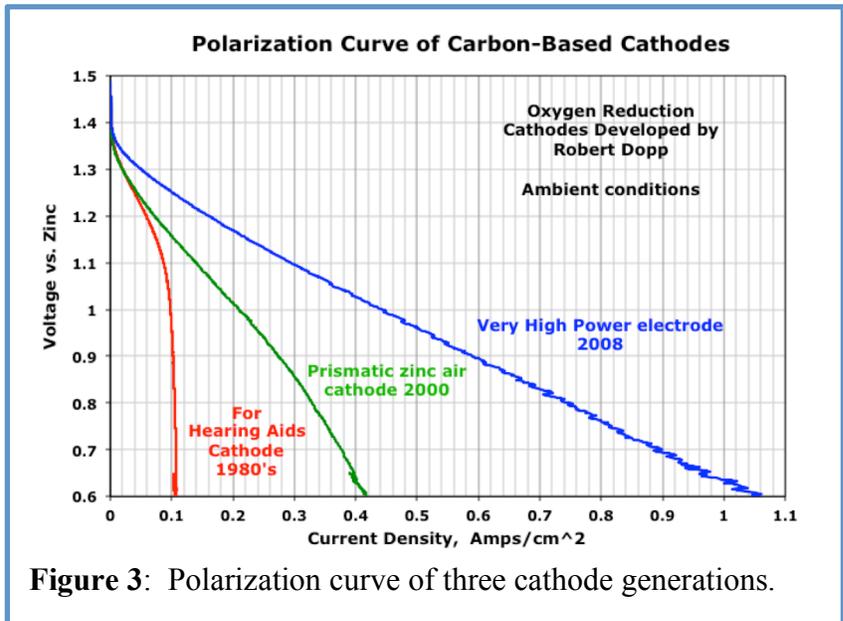- The method used for Teflon film lamination.

Testing: A half-cell apparatus was used as illustrated in **Figure 2** . It exposes exactly 1 cm^2 of surface area so power and energy density readings are read directly. A Solartron Electrochemical Interface and Frequency Response Analyzers were used to drive the potential from 25 mV above OCV to 800 mV below OCV. The reference electrode was a pure zinc wire (so all voltages reported here are versus zinc) and the electrolyte was eutectic (33%) Potassium Hydroxide (KOH). The testing conditions were ambient with a gentle (~50 x stoichiometric, or .5 l/min) forced convection. All data was then analyzed in Excel. IR compensation is never used in my data analysis. IR compensation gives falsely positive results that have little relevance to the "real" world.

Figure 2: Half-Cell Apparatus
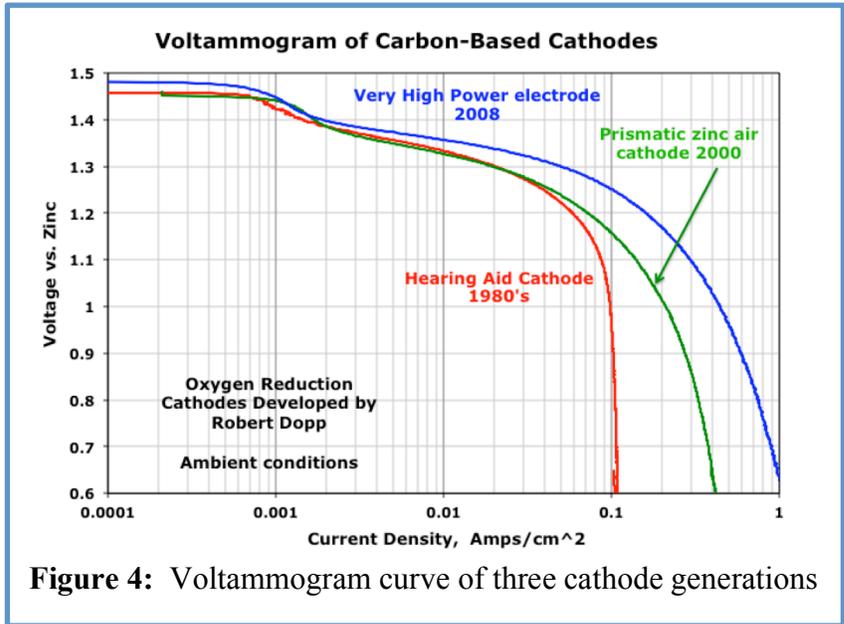
Graphic Comparison: Over the years, there were three major development Plateaus. The first was for the highest rate zinc air hearing aid battery on the market (and still is). Next was a much higher rate electrode developed for an Israeli battery company. Finally, an extremely high rate electrode was developed using a novel catalyst and several manufacturing improvements.

Figure 3: Polarization curve of three cathode generations.

The plot in **Figure 3** shows the Polarization curve, which is the voltage as a function of the current density for the three electrodes.
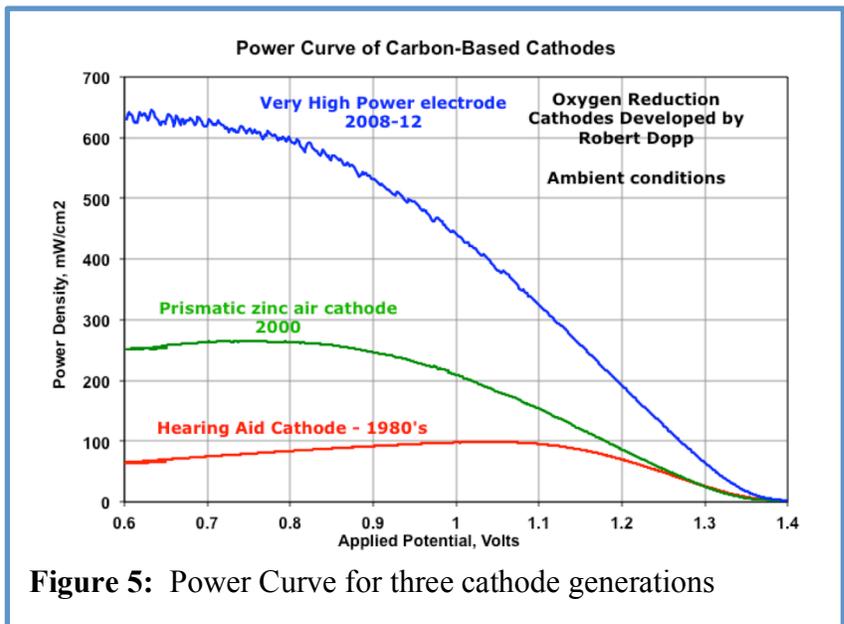
Cathode Development History.docx

Figure 4 shows a Voltammogram, which is the same as the Polarization curve, with the independent axis (current density) plotted on a logarithmic scale. This shows the electrochemical efficiency of the reaction in the linear portion called the "Tafel" region from 3 to 6 mA/cm^2 in this case). The maximum current density is called the limiting current because it is the kinetic limit of the electrode.

Figure 4: Voltammogram curve of three cathode generations

Figure 5 shows the Power density curve, where the power units are mW/cm^2 is plotted as a function of the cathode voltage. This is the most informative graph, as it shows the useful output of the electrodes. This author has never seen any data reporting power densities even close to these when run under ambient conditions.

The lower two electrodes shown are still in production today with the highest power electrode's uses still in development.

Figure 5: Power Curve for three cathode generations

Tabular comparison:
Taking several key parameters from the graphic data above, comparisons are easy to see in the tabular form of Table 1.

Regards,

Bob

	For Hearing Aids	For Prismatic Cells	High Powered Electrode
beta, mV/dec	77	68	47
Internal iR loss, Ohms	4.50	1.48	0.93
0.6 Volt Limiting Current, mA/cm^2	108	417	1061
Current Density at 1 Volt, mA/cm^2	98	209	441
Max Power, mW/cm^2	99	265	645

Table 1: Tabular Data